

锂电池失效分析与测试技术专刊

## 锂离子电池三元层状氧化物正极材料失效模式分析


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**摘要:** 镍钴锰三元层状氧化物 (NCM) 正极材料由于其优越的综合性能在动力/储能电池系统 (ESS) 领域得到广泛应用。虽然Ni含量的增加可提高三元材料的比容量及电池的能量密度, 但相关电池体系的容量保持率和安全性将会变差。如何有效解决该矛盾是此类NCM电池所面临的关键问题。本文从NCM电池体系循环过程中常见的体相结构破坏和正极-电解液界面组成改变两方面失效现象出发, 结合近年来国内外对NCM失效模式研究中所提出的新理论、方法、应用, 从机械破坏、结构演变、电化学极化、化学副反应、正负极协同效应等多个角度对NCM材料的衰退机理提出见解, 对指导电池用户合理制定充放电协议、缓解电动汽车 (EV) 里程焦虑乃至材料设计本身均有重要的指导及借鉴意义。

**关键词:** 锂离子电池; 三元正极材料; 失效现象; 老化机理; 表界面行为; 体相结构

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## Failure mechanism of $\text{Li}_{1+x}(\text{NCM})_{1-x}\text{O}_2$ layered oxide cathode material during capacity degradation

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**Abstract:** Ternary layered oxide (NCM) cathode materials are widely used in today's energy storage systems (ESS) due to their advantages of high energy/power density, high specific capacity and high oxidation-reduction potential (ORP). Cathode material specific capacity increases with the improvement of Ni content while its stability, safety and capacity retention rate are decreasing. So how to deal with this contradiction effectively is the key to develop ternary material system. This paper starts from the failure phenomenon on account of bulk phase structure destruction and cathode-electrolyte interface composition change during the cycle of NCM battery system. Combined with the new theory, new method and new application in the research of NCM failure mode at home and abroad in recent years, the possible decline mechanism and life decay reasons of mechanical damage, structural evolution, electrochemical polarization, chemical side reaction process and synergistic effect of cathode and anode electrodes are giving. The results guide users to rationally formulate

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charging and discharging protocols and alleviate electric vehicles (EV) range anxiety and the design of the material.

**Key words:** lithium ion batteries; NCM cathode material; failure behavior; ageing mechanism; surface and interface; bulk structure

在用电设备对锂离子电池能量及功率密度要求日益增长的今天,三元层状金属(Co、Mn、Ni、Al等)氧化物电极( $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ )以其高理论比容量( $>250 \text{ mA}\cdot\text{h/g}$ )及较高工作电压(约3.65 V)的特点,作为一种重要的动力电池材料被寄予厚望<sup>[1-4]</sup>。但是,对于如电动汽车、储能系统等性能导向的用户需求而言,商业化锂离子电池仍面临诸多挑战,例如,如何设计电池(组)在更宽电压区间内正常运行以提供更高能量<sup>[5]</sup>,在高/低温等滥用条件下如何保证电池组和操作者安全的硬性要求等<sup>[6-8]</sup>。正极材料的储锂能力是目前限制电池容量性能的关键,因为其容纳锂离子的能力远低于商业化石墨负极(约372  $\text{mA}\cdot\text{h/g}$ )。通过比较负极比容量、正极比容量以及提高电池电压操作区间3种情况对全电池能量密度的影响<sup>[9-10]</sup>结果如图1(a)所示,可以明显看出,正极材料是突破目前电池能量密度限制的关键所在。文献[11]曾对比NCM111、523、622、71515、811等含有不同比例过渡金属元素的正极材料电化学性能及热稳定性,从中发现,随着镍元素含量增加,电极容量增加;但当镍含量超过0.6时,电极稳定性出现明显

下降。因此,明确三元正极材料失效模式及衰退机理,对于设计及优化电池组件、设置充放电协议、延长商业化锂离子电池使用寿命是至关重要的。

## 1 NCM层状正极材料失效模式概述

通过将正极充电到更高电压的方式理论上能够提升 $\text{Li}^+$ 的利用率(即电池的有效容量),但与此同时, $\text{Li}^+$ 在层状结构中的过度脱嵌将引起结构的不稳定,导致多种副反应的发生(图2)。三元材料的失效模式与其被使用的容量存在着直接联系。在脱锂量较低的情况下,电池失效模式主要为:①由于 $\text{Ni}^{2+}$ (0.69 Å, 1Å=0.1nm,余同)和 $\text{Li}^+$ (0.76 Å)的离子半径相近且其迁移势垒较低,随着材料中Ni含量的提高,NCM材料倾向于发生较强的反位缺陷偏聚行为<sup>[12-13]</sup>,通常表现为在晶格的3b位点发生Li-Ni位置交换,出现 $\text{Li}^+/\text{Ni}^{2+}$ 混排,阻塞Li的传输通道,导致电池首效低、长期循环性能差;②由于 $\text{Li}^+$ 的脱出,为进行电荷补偿,高氧化性物种 $\text{Ni}^{4+}$ 出现,使得电解液易于在正极表面分解,消耗体系中的活性锂离子,并影响材料热稳

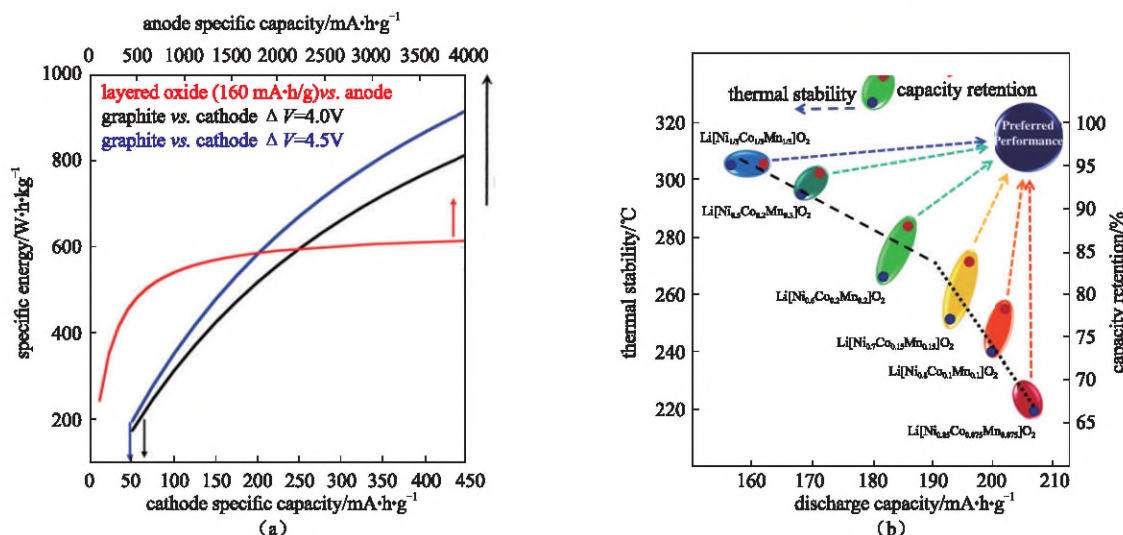


图1 (a) 仅对正极比容量(黑色曲线)、负极比容量(红色曲线)优化并在此基础上提高工作电压(蓝色曲线)后全电池能量密度变化情况示意图; (b) 不同Ni、Co、Mn元素含量三元层状正极材料放电容量、热稳定性、容量保持率综合比较<sup>[11]</sup>  
**Fig.1** (a) Full cell energy density of the modified cathode electrode material (red curve); the modified anode electrode material (blue curve) and original material with higher operating voltage; (b) A combined comparison map of  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$  ( $1-x-y=1/3, 0.5, 0.6, 0.7, 0.8, 0.85$ ) discharge capacity, thermal stability and capacity retention<sup>[11]</sup>

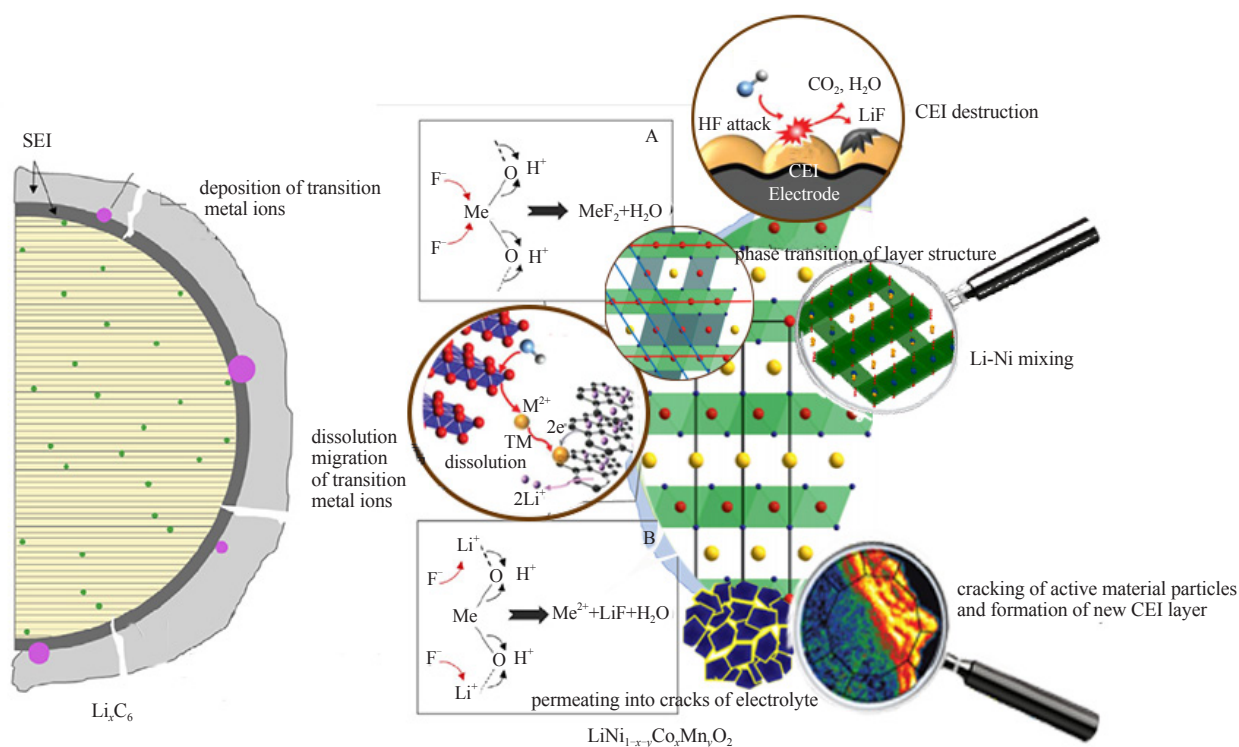


图2 NCM正极材料失效模式归纳示意图

Fig.2 An overview of failure scheme &amp; phenomenon of NCM cathode which includes

定性；③电解液中含 $H^+$ 物种攻击正极材料表面，引发电极表面过渡金属离子的溶出，导致界面非均相化学反应发生，电极界面由层状结构向立方相转变，表面形成绝缘钝化层，增大界面阻抗；同时，溶出的过渡金属离子还可能迁移至负极材料表面，在SEI膜上沉积。在脱锂量较高的情况下，新的失效模式随之出现：①相变增多引发结构破坏，局部微应力增加，诱发一次晶粒内部裂纹及二次颗粒裂缝的形成及扩展，同时生成非活性组分 $NiO$ ，进一步使体相结构无序化。当一次晶粒破坏时，电解液渗入新的微裂纹界面并形成钝化膜，造成活性锂离子损失、阻抗增加；若应力进一步破坏二次颗粒，还将影响活性材料颗粒与导电剂的接触效果；②由于过渡金属离子与 $O^{2-}$ 有能带重叠（如 $Ni$ 的 $3d$ 轨道和氧的 $2p$ 轨道），随着外加电压升高，在高脱锂态（高荷电态）下， $O^{2-}$ 被氧化，过氧物种或超氧物种形成，电极脱氧，使得过渡金属离子形成非稳定高氧化性副产物，导致界面相变发生，同时，电解液在电极表面的氧化反应活性将显著提升。

## 2 本体结构失效模式

层状过渡金属氧化物理论上具有规整的层状

$\alpha-NaFeO_2$ 型晶体结构（空间群 $R\bar{3}m$ ， $Z=3$ ）。过渡金属（TM）与 $Li^+$ 在立方密堆积的氧晶格中交替占据八面体位(图3)，而 $Ni$ 、 $Co$ 、 $Mn$ 离子根据材料配比依照统计规律分布在 $3b$ 位点上， $Li^+$ 则占据TM层间Wyckoff  $3a$ 位点。

$Ni$ 作为正极主要的氧化还原物种，含量越高则能够提供更多的可逆容量，但在深度充电过程中，也会引发更严重的结构和热的不稳定性。混排的出现使得在 $Li$ 的 $3b$ 位上出现的 $Ni^{2+}$ 倾向于与就近的 $Mn^{4+}$ ( $3a$ )发生铁磁体干扰，以 $Ni^{2+}$ ( $3b$ )缺陷为中心，形成 $Ni^{2+}$ ( $3b$ )- $Mn^{4+}$ ( $3a$ )铁磁体簇，造成电极微观结构变化<sup>[14]</sup>。 $Ni^{2+}$ 在充电过程中易被氧化为 $Ni^{3+}$ ，但由于动力学上的差异，该反应在放电时不完全可逆，因此使得部分 $Ni^{3+}$ 周围的6个 $Li^+$ 无法嵌入，不但导致容量损失、极化增大，而且造成层间结构的局部塌陷，严重影响电池寿命。 $Co^{3+}$ 的掺杂可在一定程度上抑制混排现象<sup>[15]</sup>。文献[16]比较了不同过渡金属配比（NCM523与NCM433）正极材料的长循环性能，从对其1000及2000次循环后的EIS结果可看出， $Ni^{4+}$ 在电极脱锂态下形成的非活性物种 $NiO$ 造成正极-电解液界面传荷阻抗增加，所以在相同条件下， $Ni$ 含量更高的NCM523表现出更严重的容量衰退。MU等<sup>[17]</sup>提出“反应面”的

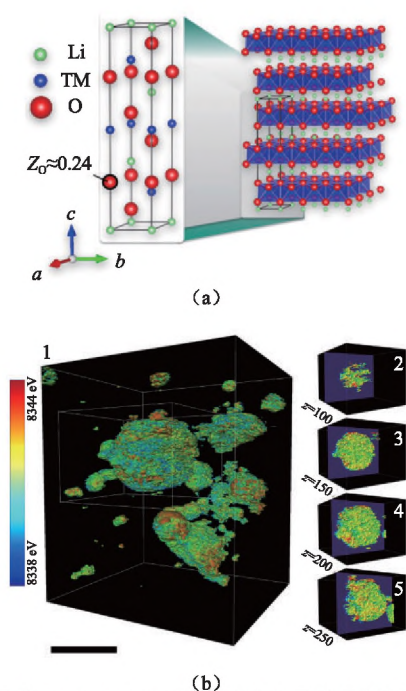
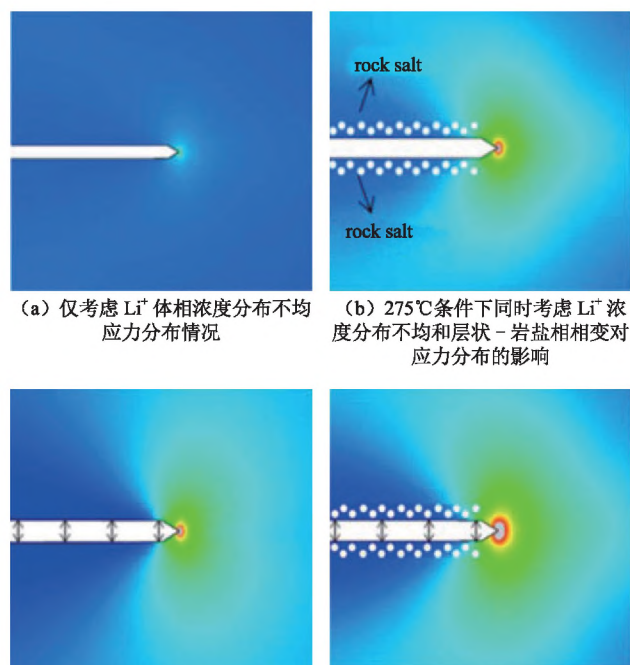


图3 (a)层状  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  材料单个晶胞晶体结构示意图<sup>[18]</sup>；(b) 1 为  $231^\circ\text{C}$  加热  $20.5\text{ h}$  后单个 NCM 二次颗粒中等价态 Ni (反应面) 三维分布图, 2~5 为单个像素体元 Ni 价态随不同深度分布情况<sup>[17]</sup>

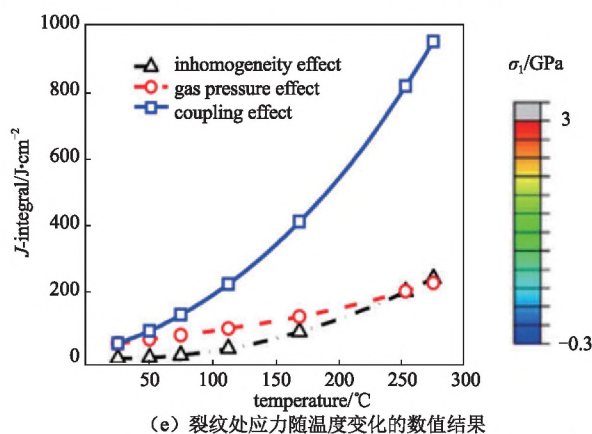
Fig.3 (a) schematic of the unit cell of layered  $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$  with crystal structure; (b) (1) three-dimensional distribution of Ni valence states (calculated by K-edge energy) over the polycrystalline ensembles after  $231^\circ\text{C}$  &  $20.5\text{ h}$  heating process; (2-5) single-voxel thick slices through different depths of a particle (30 nm thick slices at 50 voxels apart through the largest particle in (1)

概念[图3 (b)], 即借助X射线吸收光谱(XANES)成像技术观测多晶NCM在不同温度下Ni元素价态转变行为, 计算Ni K-边吸收峰峰值曲率, 发现过渡金属元素价态等值面在三维尺度上呈现出摇摆震荡现象, 证明NCM电极二次颗粒在电化学反应中的不均匀相变过程(层状-尖晶石-岩盐相)。

随着锂离子在正极活性材料颗粒内部的脱嵌, 多次的体积膨胀/收缩可能引起机械应力的累积, 在活性材料颗粒二次团聚后的一次颗粒边缘处形成微裂纹<sup>[19-21]</sup>, 导致电解液渗入, 因此, 电池性能在循环后期将快速衰减。YAN等<sup>[22]</sup>借助有限元法模拟了NCM622材料的裂纹形成与生长的电学-热学-力学耦合过程(图4), 结果表明材料颗粒体相 $\text{Li}^+$ 浓度分布不均造成化学应力在裂纹尖端聚集以及微裂纹出现的主要原因; 同时, 高压下氧离子脱出反应使得界面层状结构向岩盐相转变, 引发氧气的释放造成局部压强增加, 驱动裂纹扩展, 该反应在温度较高(实验值 $275^\circ\text{C}$ )时会



(a) 仅考虑  $\text{Li}^+$  体相浓度分布不均应力分布情况 (b)  $275^\circ\text{C}$  条件下同时考虑  $\text{Li}^+$  浓度分布不均和层状-岩盐相相对应力分布的影响 (c)  $275^\circ\text{C}$  条件下考虑由氧气释放带来的界面压力对应力分布的影响 (d) 当 (b)、(c) 所示情况同时存在时的应力分布情况



(e) 裂纹处应力随温度变化的数值结果

图4 NCM622 材料裂纹扩展驱动力的多物理场耦合有限元模拟结果

Fig.4 finite element result of NCM622 material crack propagation driven by multiple physical fields

变得更加明显。

改善本体结构失效的有效方法之一是元素掺杂。LI等<sup>[23]</sup>认为非金属元素F离子的掺杂能够造成氧缺陷, 产生过渡金属及 $\text{Li}^+$ 空位, 使 $\text{Li}^+$ 具有更加稳定的传输通道, 亦可提高材料结晶度和抑制体积膨胀, 其电荷补偿机制满足式(1)。除此之外, 目前三元材料的金属掺杂已被广泛商业化, 如少量 $\text{Mn}^{2+}$ 的存在可代替 $\text{Ni}^{2+}$ 进入Li层空位, 维持结构稳定性的同时抑制Li-Ni混排;  $\text{Cr}^{3+}$ 由于具有与 $\text{Mn}^{2+}$ 相近的离子半径, 其掺杂有利于 $d_3$ 构型的形成, 同时能够维持Mn-O键的稳定性<sup>[24]</sup>。

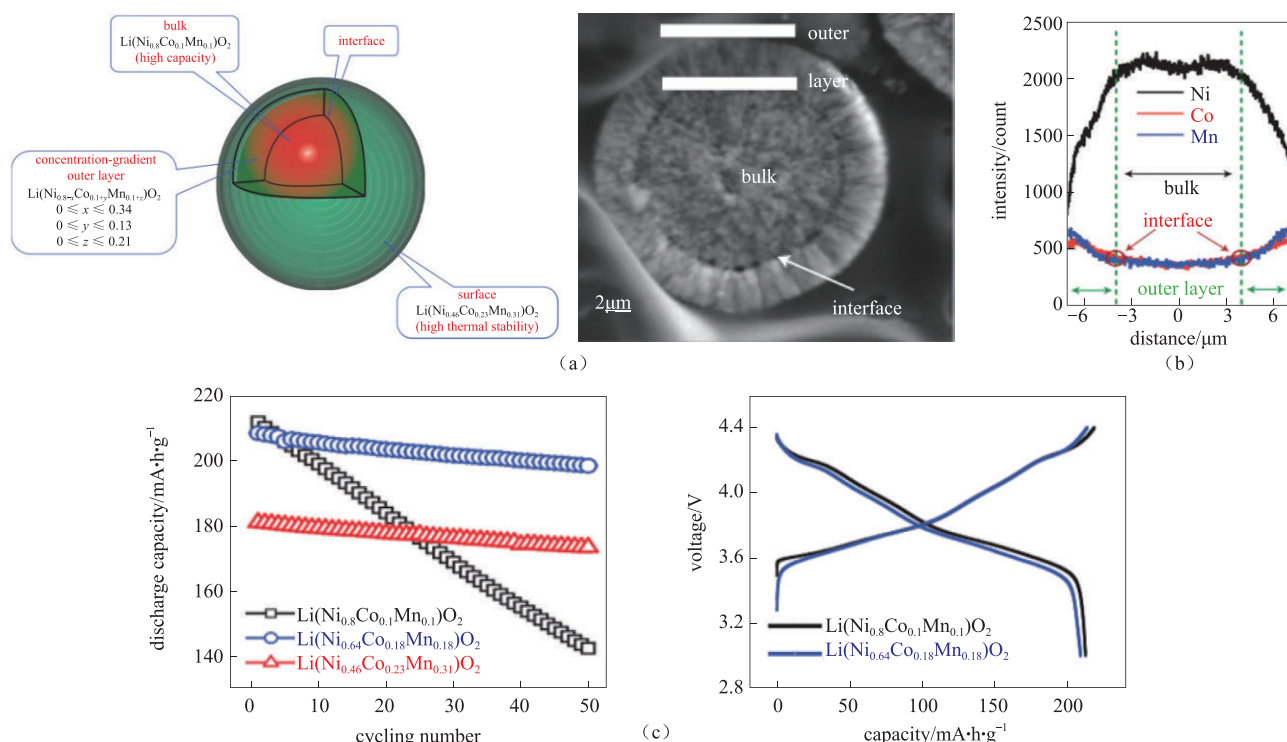
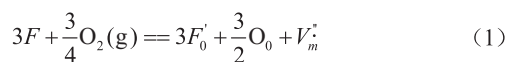


图 5 (a) 富 Mn 外壳包覆富 Ni 核浓度梯度正极材料的单粒子结构示意图及对其中任意粒子横截面的扫描电子显微镜图像，其中心体相组成为  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ ，平均组成为  $\text{Li}(\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18})\text{O}_2$ ；(b) 对最终锂化正极结构的电子探针 X 射线微区分析结果：Ni 浓度从中心向界面梯度降低、Co 和 Mn 浓度则相反；(c) 核壳结构的  $\text{Li}(\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18})\text{O}_2$  电化学性能测试结果：其容量（209 mA·h/g）与普通结构的  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$  容量（212 mA·h/g）接近，远高于  $\text{Li}(\text{Ni}_{0.46}\text{Co}_{0.23}\text{Mn}_{0.31})\text{O}_2$  容量；却具有更优异的容量保持率（55 °C，4.4 V 循环 50 次后容量为初始容量的 96%）

Fig.5 (a)schematic diagram of positive-electrode particle with Ni-rich core surrounded by Mn concentration-gradient outer layer and the scanning electron micrograph of a typical particle cross-section is showing. The core of cathode material is  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$  with an average composition of  $\text{Li}(\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18})\text{O}_2$ ; (b)the electron-probe X-ray microanalysis (EPMA) result of the final lithiation cathode material, Ni concentration decreased from the core to the interface while Co concentration and Mn concentration are contrary; (c)the electrochemical performance of  $\text{Li}(\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18})\text{O}_2$  with core-shell structure capacity (209 mA·h/g) is similar to common  $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$  (212mA·h/g), which is much higher than  $\text{Li}(\text{Ni}_{0.46}\text{Co}_{0.23}\text{Mn}_{0.31})\text{O}_2$ . And  $\text{Li}(\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18})\text{O}_2$  with core-shell structure has excellent capacity retention (the material retained 96% of its initial capacity after 50 cycles when it charged up to 4.4 V and cycled at 55 °C )



除了直接的元素掺杂外，设计浓度梯度材料也是一种既能维持材料结构稳定性和热稳定性又不牺牲电化学性能的方法<sup>[25]</sup>。SUN等<sup>[6]</sup>合成了一种内部富Ni外层富Mn的梯度材料，从活性材料颗粒本体中心向外层，其Ni浓度呈梯度降低，而Mn和Co浓度呈梯度增加[图5(a)、(b)]。其中Ni位于核内，提供高容量、保证电化学性能；Mn位于壳上，维持结构稳定性和热稳定性[图5(c)]。具有该结构的三元正极材料能够满足PHEV中能量密度需求。

原位X射线衍射或中子衍射技术是监测材料容量衰退过程中体相结构变化及失效过程的有效方法，近年来多维（时空、谱学、元素、衬度分辨）多尺度（微纳米）X射线成像技术高速发展<sup>[26-29]</sup>。

从原理上看，其对应正极过程为<sup>[30-31]</sup>：① 由于Li位的占据、消失或过渡金属的氧化还原将导致键长改变并产生晶格应变。通过对不同SOC下全电池晶胞参数原位的测试，可微观上反映出单位晶胞体积及结构的变化情况；②由于活性材料的接触损失或钝化反应将造成无法继续容纳Li<sup>+</sup>，通过分析不随充放电过程产生位移的相的比率可宏观上定量该失活部分。KINO等<sup>[32]</sup>借助波长为0.1~0.8 nm的中子束对NCM电极Bragg edges进行轰击，获得原位中子衍射成像图。该图像能够直观反映商用18650圆柱电池在不同老化条件下各组分的分布情况[图6(a)]，通过电解液在一个电池充电循环过程的迁移及电极金属Li的分布可以判断电极反应的不均匀性。经过简单的图像网格化处理，可对晶

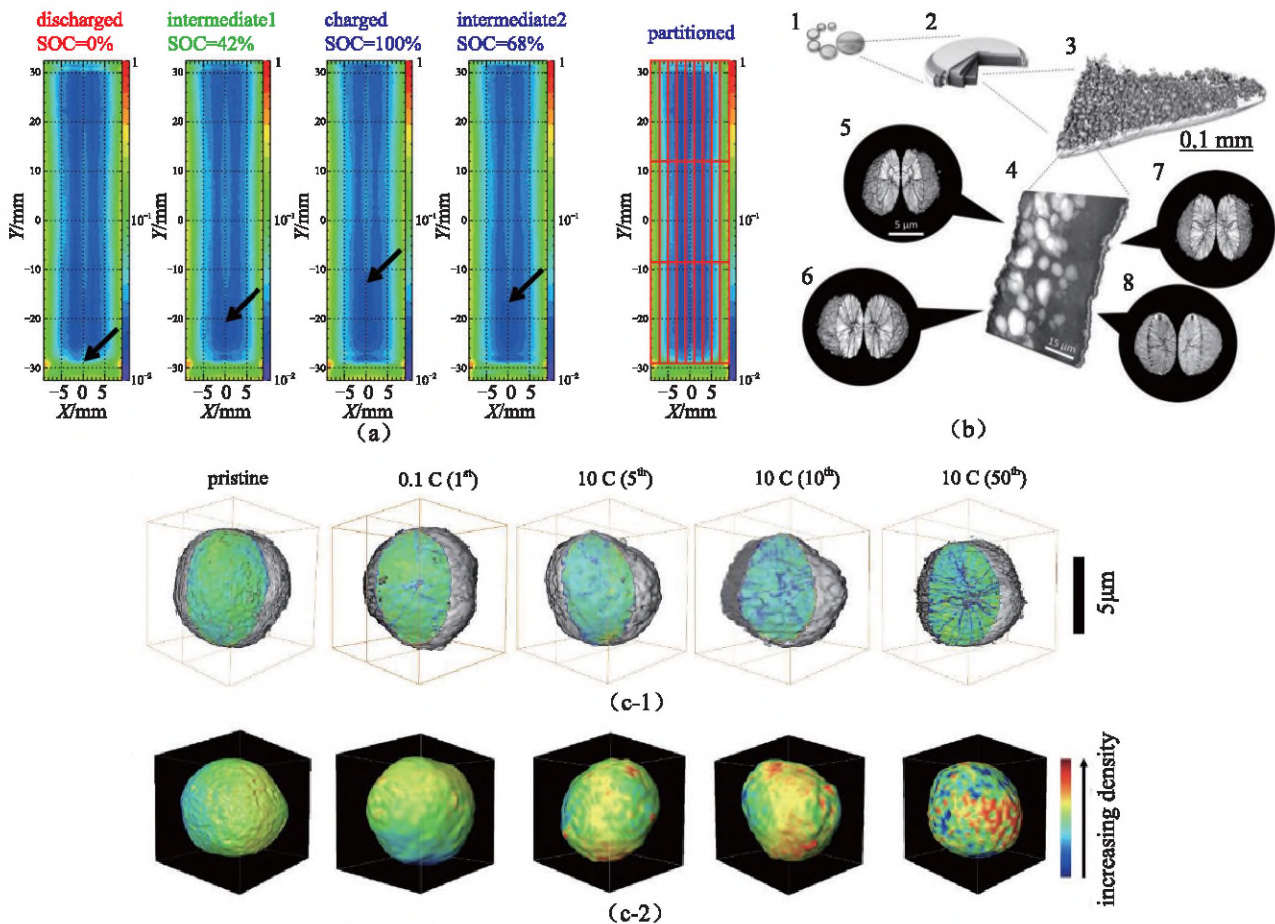


图6 (a) 0.1-0.8 nm中子波下4种充电态电极透射图像及划分网格获取Bragg edges; (b) NCM622正极材料极片X射线层析成像结果, 1~2为扣式电池结构示意, 3为正极材料X射线微区CT扫描结果, 4为正极材料纳米分辨率CT扫描结果, 5~8为对不同倍率下快充一段时间后正极材料纳米分辨率CT扫描结果; (c) c-1不同循环倍率下活性材料颗粒表面锂离子分布3D体素重构图, 突出显示粒子中心形貌缺陷; c-2活性材料颗粒表面电子负载量分布

Fig.6 (a)transmission images of the four charging states in the neutron wavelength range from 0.1 to 0.8 nm and partitioned areas for the Bragg edges analysis; (b)X-ray CT image of a random piece of NCM622 cathode, where panel 1~2 show coin cell structure; panel 3 is micro-resolution X-ray CT data; panel 4 is nano-resolution X-ray CT data; pane 5~8 are nano-resolution CT data of particles after long-time fast charging (c) 3D voxels of particles at different cycling rate accumulation history with central parts highlighted to show the morphological defects and the traffic load of electrons onto the particle surface

体表面密度进行定量分析。XIA等<sup>[33]</sup>利用X射线 nano/micro CT成像技术重现了 $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  (NCM 622) 活性材料颗粒在不同快充协议下的介观尺度微结构破坏, 由此认为, 在大电流充电情况下, 电解液向颗粒微裂纹内部渗透程度增加, 使载流子扩散路径受阻, 导致二次颗粒内局部电子电导与离子电导不匹配, 造成局部SOC不均匀, 加速了机械应力累积及裂纹的持续生长。通过多圈循环后的NCM电极断层成像分析[图6(b1~3)], 可观察到尺寸各异的颗粒随机团聚现象; 再随机选取其子区域进行纳米分辨率成像[图6(b4)], 可观察到单颗粒明显的机械不完整性[图6(b5~8)]。为了同时将倍率与循环圈数对载流子

传输路径的影响修正引入模型, 作者借助三维重构算法重现了体素图像[图6(c)], 能够直观反映出电池体相结构破坏程度。

### 3 表面失效模式

电极材料与电解液接触的不稳定性将引发多种界面非均相化学反应的发生<sup>[34-35]</sup>。随着镍元素在材料中含量的升高, 电极与电解液反应活性增强, 会使得多种离子绝缘副产物, 如 $\text{LiF}$ 、 $\text{Li}_x\text{CO}_3$ 、 $\text{LiOH}$ 等(取决于电解液成分)沉积于正极界面膜上, 阻塞 $\text{Li}^+$ 扩散路径, 影响电化学性能[图7(c)]<sup>[42]</sup>。反应后的氧化物表面还原性增强, 倾向于通过与体相原子重排的方式使表面结构进一

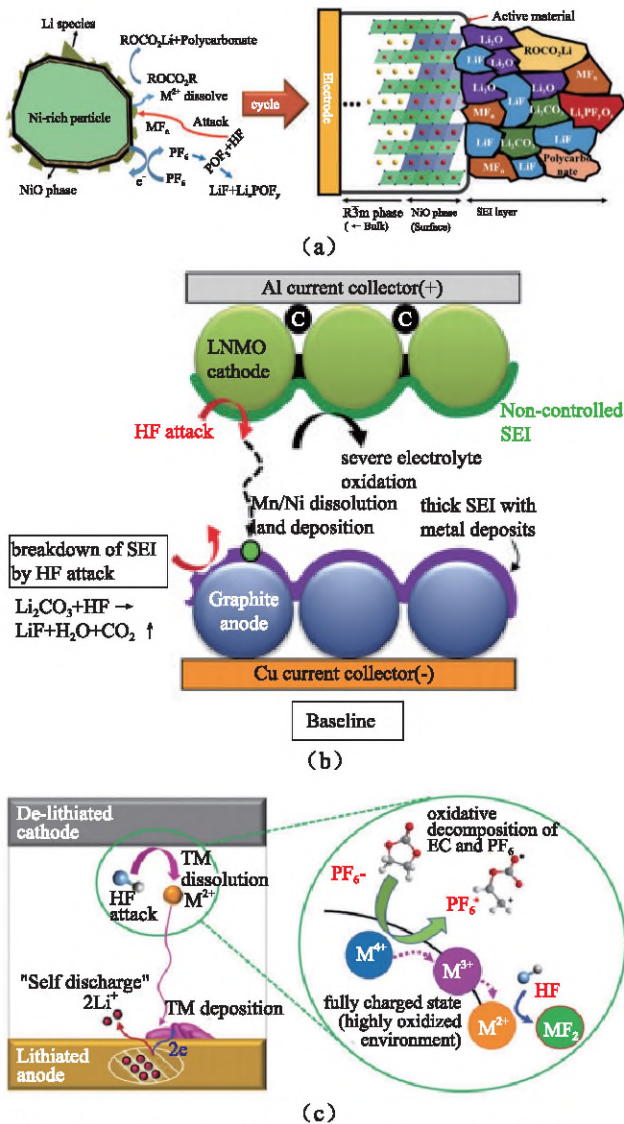


图 7 (a) 高氧化态过渡金属离子 (Mn<sup>4+</sup>, Ni<sup>4+</sup> 等) 被还原为低价离子并在正、负极界面生成阻抗较大的副产物示意图<sup>[39]</sup>; (b) 二价金属离子在负极表面沉积后引发“自放电”行为<sup>[38]</sup>; (c) 正极-电解液界面层副产物膜 (CEI) 主要成分及形成机理<sup>[42]</sup>

Fig.7 (a) higher oxidation state TM (Mn<sup>4+</sup>, Ni<sup>4+</sup>...) ions reduced to low valent ions by HF and generate by-products with large impedance at the interface on cathode and anode electrodes; (b) bivalent metal ions are deposited on the anode electrode and then cause self-discharge; (c) The main components and forming mechanism of cathode-electrolyte interface by-products (CEI)

步无序化，导致锂离子体相传荷阻抗进一步增加<sup>[36-37]</sup>。痕量的水与LiPF<sub>6</sub>发生副反应所生成的HF与电极表面的过渡金属离子反应，形成阻抗较大的产物如MnF<sub>2</sub>，造成功率损失[图7(a)、(b)]<sup>[41]</sup>，过渡金属离子将会溶于电解液并随充放电过程向负极迁移，并以金属的形式沉积在负极表面，该

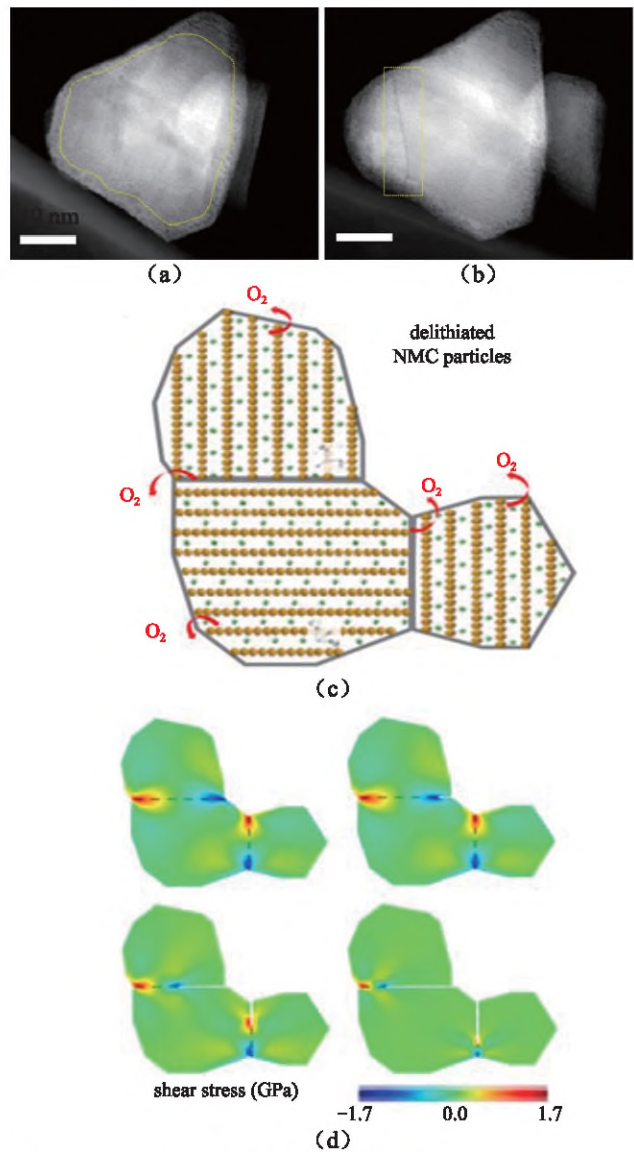


图 8 (a) 加热前期 NCM 完整一次颗粒 STEM 结果; (b) 加热后期由于失氧呈现裂纹 (黄色方框内) NCM 一次颗粒 STEM 结果; (c) 脱锂态 NCM 表面晶格脱氧机理示意图; (d) 有限元法分析 NCM 一次颗粒内部剪应力随受热时间分布变化分布<sup>[45]</sup>

Fig.8 (a) STEM images for the whole NCM primary particles before heated; (b) STEM images for NCM primary particles with crack due to deoxidization in late heating state; (c) Schematic diagram of the mechanism of delithiated NCM surface lattice deoxidize; (d) Finite element analysis of internal shear stress of NCM primary particles with the distribution of heating time<sup>[45]</sup>

行为必然会造成已嵌入的Li<sup>+</sup>被迫脱出进入电解液中，形成所谓的“自放电”过程<sup>[38,40]</sup>，造成容量损失。ANDERSON等<sup>[43]</sup>对一批18650电池进行加速储存寿命的测试结果证明，随着储存时间增加，正极材料表面CEI膜阻抗增大明显，其主要成分包括聚碳酸酯、LiF、Li<sub>x</sub>PF<sub>6</sub>型复合物和Li<sub>x</sub>PF<sub>6</sub>O<sub>2</sub>型复

合物等。

此外,在 $\text{Li}^+$ 脱嵌过程中会引起层状结构材料晶格维度的各向异性,在一次颗粒晶界处形成裂纹。随着该部分机械性破损程度的加深,裂纹向内部扩展使得二次颗粒中 $\text{Li}^+$ 的传输通道被破坏,导致材料失活<sup>[44]</sup>。MU等<sup>[45]</sup>借助透射电镜(TEM)原位观测到充电态下NCM一次颗粒在加热初期无裂纹出现[图8(a)],随着受热时间延长,裂纹线性生长并趋于平稳的现象[图8(b)]。借助有限元法计算结果,他们认为一次颗粒长期循环或高温循环过程中不断累计的表面失氧过程是诱发层状结构发生不均匀相变、晶界裂纹出现的重要原因[图8(c)、(d)]。

LIU等<sup>[46]</sup>对商业化NCM正极材料颗粒进行观测,发现其含Li相在一次颗粒内部分布未发生变化,而在界面处有明显梯度。借助原位XRD分析[图9(a)]得出,和各向同性的立方相材料相比,在相同充电条件下三元材料发生了更严重的结构破坏,随着电压升高,电解液的分解加剧,其循环性能却并未受到很大影响。因此,对于层状正极材料非高压长循环过程而言,物理晶间破

裂是比电解液分解更为重要的容量衰减因素。在对团聚结构的三元材料设计过程中应尽量减小一次颗粒尺寸,以分担由各向异性变化引起的晶界应力。潘锋课题组<sup>[47]</sup>借助第一性原理计算提出NCM三元材料的热不稳定性主要与发生在界面的氧反应有关,而氧原子的局部配位单元(LSCU)决定了其反应活性[图9(b)~(d)]。一旦表面出现空位,不饱和氧原子反应活化能迅速降低,与体相相比具有更高的不稳定性,使表面氧反应过程以更快速度推进。NCM材料在 $300\text{ }^\circ\text{C}$ 不同SOC下的(003), (018)和(110)晶面的原位XRD结果证明了Li空位出现 $\rightarrow$  Ni价态升高 $\rightarrow$  氧晶格稳定性降低这一协同作用机制对层状结构热稳定性负面效应。

在电池管理系统中常面临动力电池误用或滥用的情况,导致电池(组)过充或过放行为的发生<sup>[48]</sup>。这是因为电解液在高压下更倾向于在正极被氧化伴随着的表面氧的缺失将引发晶格畸变和裂纹生长,随着循环过程进行,混排行为会向层状结构内部扩展,引发严重的结构破坏,使层状结构向岩盐相转变<sup>[36, 49]</sup>,进一步促使过渡金属溶

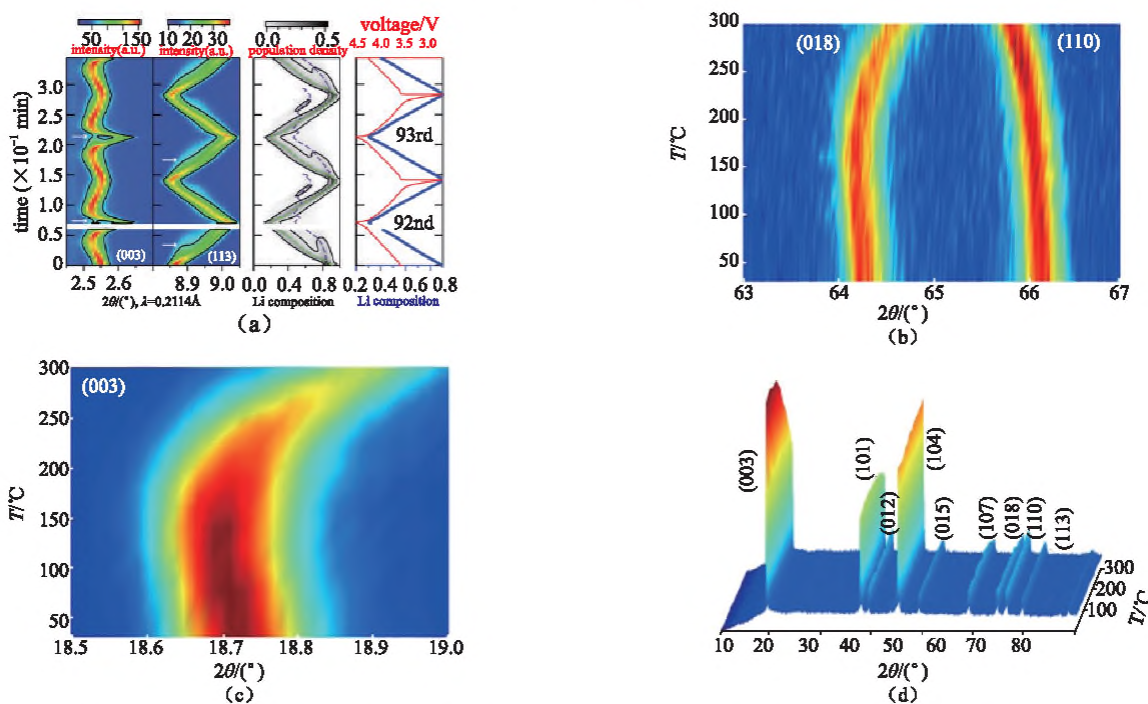


图9 (a) NCM正极材料(003)(113)晶面衍射峰强度等高图<sup>[46]</sup>; (b) 活性(绿色虚线)及非活性(紫色虚线)含Li相分布; (c) 电极电势分布(红)及平均含Li相(蓝)构成定量分布结果<sup>[47]</sup>

Fig.9 (a) Contour plots of (003) and (113) crystal plane diffraction peak intensity (black line)<sup>[46]</sup>; (b) Distribution of the Li composition, the active material (dashed green line) and sluggish material (dashed purple line); (c) The distribution of corresponding voltage profile (red line) and the quantified distribution of average Li composition (blue line)<sup>[47]</sup>



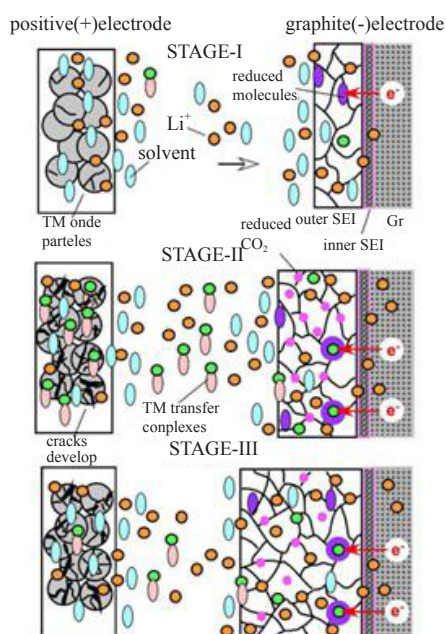


图10  $Mn^{2+}$  溶出-迁移-沉积耦合SEI生长动力学示意图<sup>[51]</sup>  
 Fig.10 Growth dynamics schematic diagram of  $Mn^{2+}$  dissolution, migration and deposition coupling with SEI<sup>[51]</sup>

出的发生并通过电解液向负极迁移，影响负极SEI的组成<sup>[50]</sup>。有研究者<sup>[51]</sup>认为，过渡金属的溶出-迁移-沉积机理实际可以分为三个阶段（图10）：  
 ①“诱导”阶段：过渡金属离子开始溶出，并自发迁移至SEI内层（无机层）表面，发生少量沉积，若该沉积与来自负极界面的电子接触，还原产物将作为电催化剂<sup>[52]</sup>或SEI的电子通道<sup>[53]</sup>，使更多活性锂被SEI捕获，加速电池容量损失；  
 ②快速沉积阶段：裂纹在正极活性材料颗粒内部扩展，溶出量增加，过渡金属离子与电解液溶剂分子结合形成复合体并大量沉积在SEI外层（有机层）表面，致使SEI层厚度显著增加；  
 ③平稳阶段：当SEI增加到一定厚度时，由于其表面可占据的活性锂位减少，沉积速度趋于平缓。

设计正极-电解液界面以提高氧化物活性表面与电解液接触界面稳定性，如采取纳米粒子包覆NCM材料或原子层沉积氧化物的方法，本质上是提高界面反应能垒，减少了过渡金属离子的溶出<sup>[54-56]</sup>。CHEN等<sup>[57]</sup>将钛酸盐溶解于无水乙醇中，利用水解法成功地将 $TiO_2$ 包覆在纳米尺度的 $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ 材料表面，修饰后的电极表现出良好的循环性能、倍率性能和热稳定性。1%（质量分数） $TiO_2$ 修饰的 $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ 电极材料在4.5 V截止电压，1 C充放电倍率的条件下，经过50次循环后容量保持率为88.7%，比相同条件

下未修饰的电极（78.1%）有了显著改善。他们认为， $TiO_2$ 层一方面能够抑制正极与电解质之间的界面反应，稳定界面并减少循环过程中的阻抗增长；同时，也能防止正极材料分解，从而提高材料的结构稳定性。KIM等<sup>[58]</sup>使用双导电聚（3,4-亚乙二氧基噻吩）-聚乙二醇（PEDOT-co-PEG）共聚物对 $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ 正极改性，结果表明在55 °C和0.5 C的放电条件下，改性后的正极材料较未改性的材料表现出更优异的循环性能。

用金属氧化物（如 $Al_2O_3$ 、 $MgO$ ）对正极材料进行包覆，能够修饰表面电子结构及电势分布，稳定电化学反应。与直接裸露在电解液中相比，该包覆过程可以使过渡金属离子在复合后的电极材料表面更不易被还原<sup>[59]</sup>。然而，由于包覆层离子绝缘且流动性差<sup>[60-61]</sup>，锂离子的扩散也会同时受到限制，所以往往还应进行额外操作处理，如溅射或退火，使包覆层与正极材料化学结合带有载流子（通常为 $Li^+$ ）。孙学良课题组<sup>[62]</sup>采用溶胶凝胶法在NCM材料上包覆了增强离子传导性的铝酸锂薄膜，和不具备离子传导性的 $Al_2O_3$ 相比，两者能够对NCM材料结构不稳定性、金属离子的溶解和电解质的分解起到改善作用，但是超薄可控的 $LiAlO_2$ 层对正极材料循环稳定性和倍率性能方面的改善要优于 $Al_2O_3$ 。美国Argonne国家实验室CABANA课题组<sup>[63]</sup>通过原子层沉积包覆法进一步证实了这一结论。

电解液的设计优化是另一种维持正极材料界面稳定的方法，从机理上大致可分为两类<sup>[64-65]</sup>：  
 ①用额外的吸电子基团对溶剂分子进行取代，以降低其最高占据轨道（HOMO），从而有效提高电解液自身的高压稳定性<sup>[66-67]</sup>；  
 ②通过向电解液中添加牺牲添加剂，形成表面钝化膜以阻隔电解液与正极材料活性位点的直接接触<sup>[68-74]</sup>。DAHN课题组<sup>[75-76]</sup>通过对比全电池与电极/电解液界面的EIS阻抗谱结果发现，在NCM523/石墨电池体系循环后期出现的容量“跳水”主要与正极/电解液界面传荷阻抗的增加有关，而负极/电解液界面的阻抗在“跳水”前后几乎保持不变；充电曲线终点随循环过程的位移证明，随着充电截止电压提高和电流增大，电解液在正极界面的氧化过程将会加快，借助超高精度库仑效率分析（UHPC）发现容量“跳水”的出现时间与电极液在正极材料表面的氧化耗尽直接相关。

#### 4 三元层状正极材料失效对电池容量衰退的影响

与磷酸铁锂正极材料脱嵌锂离子时所发生的两相反应不同<sup>[77]</sup>,在三元材料中发生的固溶体反应(一说连续相变反应)充放电曲线不会有明显和稳定的平台,其容量衰退过程往往与负极为行为相互耦合,使得对正极衰退机理的单独分析十分困难<sup>[78]</sup>。文献[79]、[80]和[81]分别从电化学模拟和实验测试的角度定义了NCM三元-石墨电池在长循环中容量衰减的三个阶段及正极材料失效在其中的贡献。LI等<sup>[80]</sup>通过对比商业化NCM111圆柱电池在循环过程中峰值功率(PP)及极化电阻增量(IPR)的变化,认为在第一阶段(50次循环以内),由于循环初期极化电阻较小, $\text{Li}^+$ 传输动力学较快,负极界面SEI形成及生长所造成的活性锂离子损失(loss of lithium inventory, LLI)是容量损失的主因,而此阶段正极状态相对稳定;

在第二阶段,由于SEI生长持续消耗活性锂离子,导致正极材料在放电时无法被完全利用,由此产生了去锂化<sup>[82-83]</sup>正极活性材料损失(loss of active material,  $\text{LAM}_{\text{dePE}}$ ),该损失与LLI同时发生,极化电阻增加,老化程度以较快速度进行;在第三阶段,正极 $\text{LAM}_{\text{dePE}}$ 在程度上超过负极LLI,造成正负极容量不匹配程度的累加,电池无法充分放电,部分可循环 $\text{Li}^+$ 位于石墨内部无法脱出,因此在此阶段,容量损失体现为正极活性材料损失 $\text{LAM}_{\text{PE}}$ 、锂化负极活性材料损失 $\text{LAM}_{\text{LiNE}}$ 与LLI的共同作用,引起电池中可循环 $\text{Li}^+$ 减少<sup>[84]</sup>,电池老化过程快速进行。

此三个阶段在三元电池循环曲线上通常表现出宏观容量衰减“快-慢-快”现象[图11(a)、(b)]。WHITE等<sup>[79]</sup>从单粒子(SP)模型的微观电化学参数变化中亦给出相同证据:图11(c)看出正极可利用活性材料比例随循环始终下降;由图11(d)可清晰看出老化的三个阶段,1、2区域的转折点

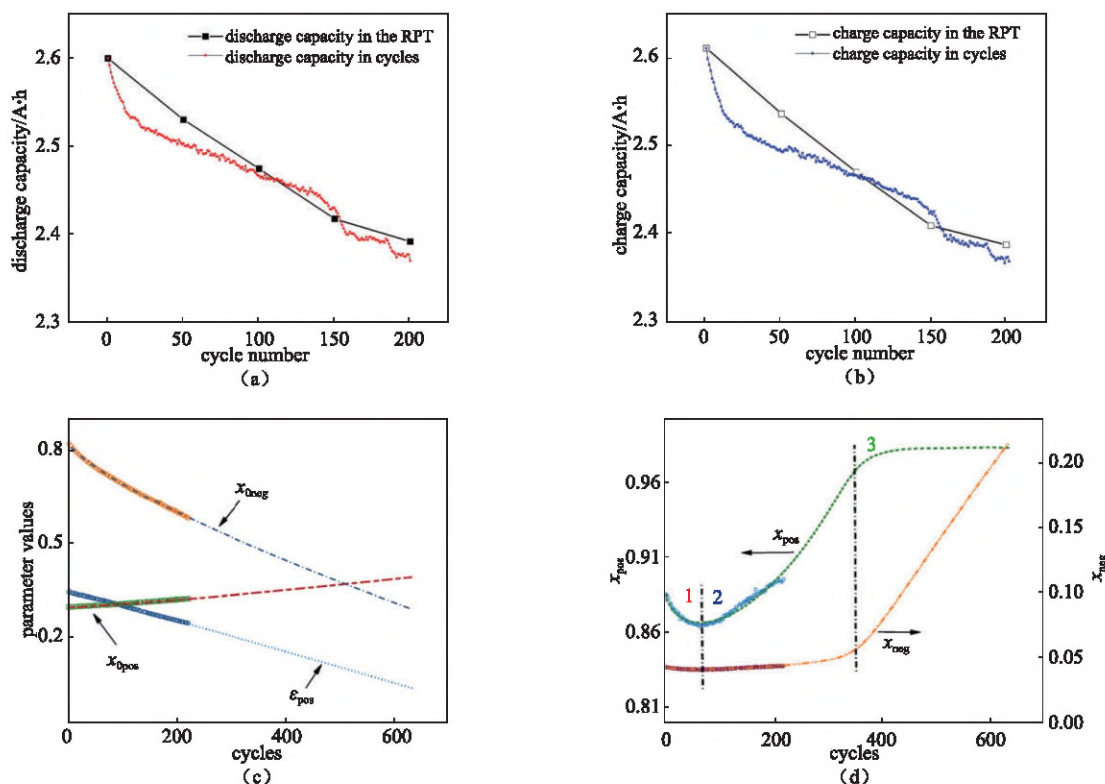


图11 动态应力测试(DST)测试协议下:(a)放电容量;(b)充电容量随循环圈数变化关系;(c)正、负极充电态下化学计量数( $x_{\text{pos}}$ ,  $x_{\text{neg}}$ )及正极活性物质占电极材料体积分数( $\epsilon_{\text{pos}}$ )随循环圈数变化情况(d)正、负极放电态下化学计量数( $x_{\text{pos}}$ ,  $x_{\text{neg}}$ )<sup>[79]</sup>

Fig.11 Under the dynamic stress test (DST) test protocol: (a) discharge capacity; (b) charge capacity of various cycle numbers; (c) stoichiometric number( $x_{\text{pos}}$ ,  $x_{\text{neg}}$ )and the fraction of cathode active material on the electrode's volume ( $\epsilon_{\text{pos}}$ ) after the various cycle numbers in cathode state and anode charge state; (d) stoichiometric number in cathode and anode electrode discharge state( $x_{\text{pos}}$ ,  $x_{\text{neg}}$ )<sup>[79]</sup>

(最低点)是 $LAM_{PE}$ 速度开始超过LLI的标志;而在区域3中, $Li^+$ 在负极化学计量数快速增加,对应于 $Li^+$ 被滞留于负极中无法回到正极,同时正极材料损失仍在加深,二者共同作用使电池加速到达寿命终点。

有研究者<sup>[85-86]</sup>基于不同测试条件,采用半经验模型对NCM电池容量衰退规律进行模拟,旨在忽略复杂内在机理演变过程,强调使用条件(温度、荷电状态、循环区间、电流密度等)对循环和储存过程的影响。在定性方面,研究表明高温循环过程将导致更早的容量跳水行为;长期深度循环会较大程度地缩减使用寿命;而电流密度对电池循环影响情况较复杂,其在循环时间和循环圈数尺度下对应电极过程零级反应和多级反应速率具有协同时变效应。对日历寿命来说,在更高的SOC(>50%)下储存的电池倾向于更快地到达寿命终止点(EOL)。BARRÉ等<sup>[87]</sup>认为其原因是当SOC较高时,将会有较大电势差作为副反应驱动力存在于电极-电解液界面,使自放电行为以更快的速度发生。在定量方面,Arrhenius温度修正的多维回归分析是一种常见的方式,以此拟合的高阶多项式可结合不同使用条件及时间预测电池容量<sup>[88-89]</sup>。除此以外,HUGGINS等<sup>[90]</sup>基于Gibbs相律提出,当 $Li^+$ 行为“固定”于相变区域,电位曲线会有平台出现;当 $Li^+$ 行为处于固溶体区域,电位曲线会有斜率出现。因此,差分电压曲线(DV)峰会在单相区增强,而容量增量曲线(IC)峰在两相区增强,结合二者信号峰的变化情况,可以在不需拆解电池的情况下诊断其 $LAM_{PE}$ 、LLI、欧姆阻抗( $R_{ohmic}$ )及法拉第阻抗( $R_{faradic}$ )变化情况。近年来,借助机器学习方法探究IC及DV特征峰变化的规律,解释NCM电极老化机理和预测电池容量衰退的方法也得到了广泛应用<sup>[78,91-92]</sup>;LI等<sup>[93]</sup>引入高斯滤波器改进传统的移动平均算法,平滑了由大量测试数据引起的噪声,精确拟合出不同区间内各个特征点坐标随电池老化的变化规律,据此可由IC曲线估算NCM523电池在任意使用状态下的SOC。

## 5 结语与展望

三元锂离子电池中正极材料的失效模式是一个复杂的行为,尽管我们基于实验现象对其从本体和界面两方面进行了归纳和总结,但在实际使用过程中,即使在最温和的使用条件下,三元正极材料

的失效过程也不是单一存在的,随着材料镍含量的提高、工作电压的提升,多尺度(体相结构、二次颗粒、电极)、多形态(本体固相、固液界面、产气)的失效模式将更多地耦合在一起。

在目前对锂离子电池正极层状材料的研究中,值得进一步关注的课题包括以下几个。①高镍层状NCM材料的热稳定性和安全性问题。随着Ni含量增高,材料在高温及高电压下的热稳定性难以维持,一旦正极发生析氧反应,析出的氧原子/氧气将与电解质有机溶液发生反应,产生其它气体并释放大量的热,致使电池体积膨胀,引发或加剧界面副反应,造成电池安全性能下降。当产生的热量不能及时转移时,还会引发自加热副反应,致使电池温度快速升高,引起内短路或热失控,严重时导致电池燃烧与爆炸。因此,发展先进的表征技术监测体系放热情况或有效的模型方法预测体系热失控现象,提出相应的处理预案,则可帮助我们降低因电池热稳定性问题导致安全事故发生的频率。②发展“去Co化”新型正极材料体系。在传统认知中,Co元素能够抑制电极材料(特别是当Ni含量较高时)中Li-Ni混排现象,有助于维持层状结构稳定,改善长循环性能。然而,Co对材料热稳定性几乎没有贡献,且在全球范围内储量有限、价格昂贵,预计到2030年以后,其供应量短缺将无法避免<sup>[94]</sup>。因此,对层状正极来说,Co是否为稳定材料结构的最佳选择已逐渐开始被人们关注和质疑。用廉价的Al、Mg或其他常用的过渡金属元素对其进行部分或全部取代,经过合理的优化设计,或有潜力合成出兼具结构稳定性和热稳定性的新材料体系。③发展与高镍材料匹配的高稳定性电解质材料,如高盐的阻燃电解质体系,或具有良好电化学/机械稳定性的固体电解质体系也将是高能NCM电池研究的重要研究课题。④借助先进的原位表征技术及模拟仿真手段获取难以利用常规实验方法直接测量的电化学参数,定性或定量地分析其随循环过程的演变规律,有助于深入理解微观反应动力学机理,进而发展出更加合理的电池寿命预测模型。

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